Density of States Approach to Electric Field Fluctuations in Composite Media

D. Cule and S. Torquato
Princeton Materials Institute, Princeton University, Princeton, New Jersey 08544
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Spatial fluctuations of the local electric field induced by a constant applied electric field in composite media are studied analytically and numerically. It is found that the density of states for the fields exhibit sharp peaks and abrupt changes in the slope at certain critical points which are analogous to van Hove singularities in the density of states for phonons and electrons in solids. As in solids, these singularities are generally related to saddle and inflection points in the field spectra and are of considerable value in the characterization of the field fluctuations. The critical points are very prominent in dispersions with a regular, "crystal-like", structure. However, they broaden and eventually disappear as the disorder increases.

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In the study of heterogeneous materials, the preponderance of work has been devoted to finding the effective transport, electromechanical and mechanical properties of the material [1], which amounts to knowing only the first moment of the local field. When composites are subjected to constant applied fields, the associated local fields exhibit strong spatial fluctuations. The analysis and evaluation of the distribution of the local field has received far less attention. Nonetheless, the distribution of the local field is of great fundamental and practical importance in understanding many crucial material properties such as breakdown phenomenon [2] and the nonlinear behavior of composites [3]. Much of the work on field distributions has been carried out for lattice models using numerical [4,5] and perturbation methods [6]. Recently, continuum models have been also addressed using numerical techniques [7].

In this Letter, we study the local electric field fluctuations by analyzing the density of states for the fields. To illustrate the procedure, we evaluate the density of states for three different continuum models of dielectric composites: the Hashin-Shtrikman (HS) construction [8], periodic and random arrays of cylinders. It is found that the density of states for the fields exhibits sharp peaks and abrupt changes in the slope at certain critical points which are analogous to van Hove singularities in the density of states for phonons and electrons in solids. This analogy is new and powerful, and places the study of field fluctuations in composites on the firm foundation of solid-state theory. In the case of the Hashin-Shtirkman construction, we obtain an exact analytical expression for the density of states. We first describe the basic equations and then determine the density of states for the aforementioned examples.

Consider a composite material composed of $(n-1)$ isotropic inclusions with dielectric constants ϵ_i and volume fractions ϕ_i $(i = 2, \ldots, n)$ in a uniform reference matrix of dielectric constant ϵ_1 with volume fraction ϕ_1. Clearly, the local dielectric constant at position $\mathbf{r}$ is $\epsilon(\mathbf{r}) = \sum_{i=1}^{n} \epsilon_i I^{(i)}(\mathbf{r})$, where $I^{(i)}(\mathbf{r})$ is the characteristic function of phase i which has non-vanishing value $I^{(i)}(\mathbf{r}) = 1$ only if $\mathbf{r}$ lies inside the volume V_i occupied by phase i. Let $\mathbf{E}_0(\mathbf{r})$ denote an applied electric field. The local electric field $\mathbf{E}(\mathbf{r})$, and the dielectric displacement $\mathbf{D}(\mathbf{r})$ are related via the relation $\mathbf{D}(\mathbf{r}) = \epsilon(\mathbf{r})\mathbf{E}(\mathbf{r})$. The potential field $u(\mathbf{r})$ is related to $\mathbf{E}$ by $\mathbf{E}(\mathbf{r}) = -\nabla u(\mathbf{r})$. The local fields are obtained from the solution of the governing relation $\nabla \cdot \mathbf{D}(\mathbf{r}) = 0$ subject to appropriate boundary conditions.

Since the local dielectric constant of the composite material is a piecewise continuous function, we can solve the following equivalent equations:

$$\nabla^2 u(\mathbf{r}) = 0, \qquad \mathbf{r} \in V_i, \tag{1}$$

$$u(\mathbf{r})|_{\mathbf{r}^-} = u(\mathbf{r})|_{\mathbf{r}^+}, \qquad \mathbf{r} \in \partial V_i, \tag{2}$$

$$\epsilon_i \partial_n u(\mathbf{r})|_{\mathbf{r}^-} = \epsilon_j \partial_n u(\mathbf{r})|_{\mathbf{r}^+}, \qquad \mathbf{r} \in \partial V_i, \tag{3}$$

where $i = 2, \ldots, n$. The index j denotes neighboring phases in contact with a given inclusion i. We donote the outward normal derivative to the interface ∂V_i by ∂_n and the interface points approached from inside or outside inclusion by $\mathbf{r}^-$, and $\mathbf{r}^+$, respectively. The numerous interfaces between the inclusions and matrix are, in general, irregular and randomly distributed in space. In most cases solutions of (1)-(3) can be found only numerically.

In order to show the salient features of the field distribution, we first consider an analytically tractable model of composite media: the HS composite-cylinder construction [8]. Although the effective dielectric constant ϵ_e of this model is known exactly, its local field distribution has heretofore not been investigated. The HS two-phase model is made up of composite cylinders consisting of a core of dielectric constant ϵ_2 and radius a, surrounded by a concentric shell of dielectric constant ϵ_1 and radius b. The ratio $(b/a)^2$ equals the phase 2 volume fraction ϕ_2 and the composite cylinders fill all space, implying that there is a distribution in their sizes ranging to the infinitesimally small. For this special construction, it is enough to consider the electric field within a single

composite cylinder in a matrix having the effective dielectric constant $\epsilon_e = \epsilon_1[1 - 2a^2\beta/(a^2\beta + b^2)]$, where $\beta = (\epsilon_2 - \epsilon_1)/(\epsilon_2 + \epsilon_1)$. Let the constant applied field point in the x-direction, $\mathbf{E}_0(\mathbf{r}) = E_o\hat{\mathbf{x}}$. Under this condition, the presence of the composite cylinder does not change the distribution of the fields in the composite for $r > b$ nor the total energy stored in the region occupied by the cylinder.

Within a cylindrical inclusion, the solution of (1)-(3) with the boundary condition $u(\mathbf{r}) = -E_0 r\cos(\theta)$ reads

$$u(\mathbf{r}) = \begin{cases} Ar\cos(\theta), & \text{for} \quad r \le a, \\ (Br + \frac{C}{r})\cos(\theta), & \text{for} \quad a \le r \le b. \end{cases} \tag{4}$$

Consequently, the magnitude of the electric field is constant $|\mathbf{E}(\mathbf{r})| = |A|$ for $r \le a$, and

$$|\mathbf{E}(\mathbf{r})| = |B|\sqrt{1 + (\frac{a}{r})^4\beta^2 + 2\beta(\frac{a}{r})^2\cos(2\theta)} \tag{5}$$

for $a \le r \le b$. The coefficients A,B, and C depend on the geometry and material properties:

$$A = E_0(1-\beta)/(\beta\phi_2 - 1), \tag{6}$$
$$B = E_0/(\beta\phi_2 - 1), \tag{7}$$
$$C = E_0 a^2\beta/(\beta\phi_2 - 1). \tag{8}$$

In the study of electric-field fluctuations, it is convenient to introduce a density of states per unit volume, $g(E)$, defined so that $g(E)dE$ is the total number of states in the range between E and $E+dE$, divided by the total volume of the inclusion:

$$g(E) = \frac{1}{\pi b^2}\int \delta(E - |\mathbf{E}(\mathbf{r})|)d\mathbf{r}. \tag{9}$$

Substituting (5) into (9) yields

$$g(E) = \phi_2\delta(E - |A|) + \frac{2\phi_2 E}{\pi B^2}\int_{\phi_2}^{1} dx \frac{1}{x^2\sqrt{\gamma_E(x)}}\Theta\big(\gamma_E(x)\big), \tag{10}$$

where $\Theta(x)$ is the Heaviside step function, and

$$\gamma_E(x) = 4(\beta x)^2 - [1 + (\beta x)^2 - (E/B)^2]^2. \tag{11}$$

We note that $\gamma_E(x)$ is bounded from above, and that the integrand in Eq. (10) is non-zero only if $\gamma_E(x) \ge 0$, implying that the density of states $g(E)$ is non-zero only for fields in the finite *bandwidth*: $E \in [E_{\rm min}, E_{\rm max}]$. The extremal field values for the problem at hand are $E_{\rm min} = |B|(1 - |\beta|)$, and $E_{\rm max} = |B|(1 + |\beta|)$.

The highest field determines the electrical breakdown properties. Equally important are the fields at which $g(E)$ has its maxima, i.e., the fields that occur most frequently in the composite. To identify them, note that the dominant contributions to the integral in (10) come from regions close to the points $x_0 = |\beta|^{-1}|1 \pm |E/B||$ which are solutions of $\gamma_E(x_0) = 0$. Expanding $g(E)$ about x_0, and integrating (10) yields $g(E) \sim (x - x_0)^{1/2}|^1_{x_0=\phi_2}$ or $g(E) \sim [(1 - x_0)^{1/2} - (\phi_2 - x_0)^{1/2}]$. Thus, the density of states $g(E)$ is not an analytic function since its derivatives are singular at $E = E_{VH}$ for which $x_0 = 1$ or ϕ_2:

$$E_{VH} = \begin{cases} E_{\rm min}, \\ |B||1 - \beta\phi_2|, \\ |B||1 + \beta\phi_2|, \\ E_{\rm max}. \end{cases} \tag{12}$$

These singularities are very similar to the van Hove singularities found in the density of states for phonons and electrons in solids [9]. As in the case of solids, the singularities in $g(E)$ are gernerally associated with saddle and inflection points on the surface of generated fields $|\mathbf{E}(\mathbf{r})|$. At these points, $g(E)$ exhibits characteristic sharp local maxima or minima, with abrupt changes in the slope. This is illustrated in Figs. 1 and 2. Because the HS construction lacks translational symmetry (unlike the subsequent period example), only inflection points are present

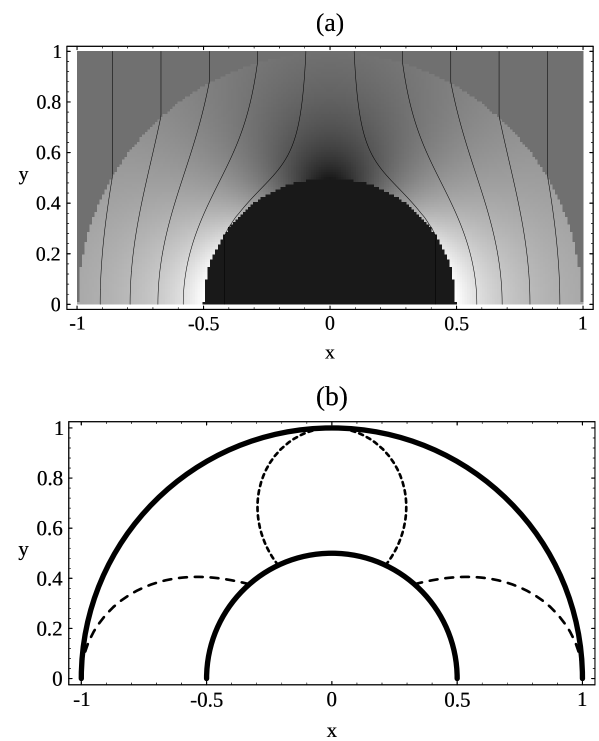

FIG. 1. The upper half of a composite cylinder of outer radius $b = 1$ with inner core of radius $a = 0.5$ (i.e., $\phi_2 = (a/b)^2 = 0.25$), dielectric constant $\epsilon_2 = 10$, and outer concentric shell of dielectric constant $\epsilon_1 = 1$: (a) Electric field density plot in which lighter shades (gray-scale representation) correspond to increasing field magnitudes, and associated contours of equipotential lines $u(\mathbf{r})$ = const. (b) Distribution of fields contributing to van Hove singularities in the density of field states $g(E)$. Dotted lines show positions of $E_{VH} = |B||1 - \beta\phi_2| = E_0$ while dashed lines identify $E_{VH} = |B|(1 + \beta\phi_2)$. The thick lines denote the boundaries of the cylinders.

in the density plot of $|\mathbf{E}(\mathbf{r})|$ shown in Fig. 1(a). They occur in phase 1 along the lines $\theta = 0$ and $\theta = \pi/2$.

Figure 1(a) shows the density plot of local electric fields together with the contours of the equipotential lines. Inside $r \leq a$ region, the magnitude of electric field is constant. This generates the δ-function in the density of states (10). To locate spatial coordinates of the singular fields E_{VH}, we first consider the case $\epsilon_2 > \epsilon_1$. From Eq. (5) it follows that $E_{VH} = E_{\text{min}}$ where $(r = a, \theta = \pi/2)$. Since $E_{\text{min}} = |A|$, the position of this van Hove singularity overlaps with position of the δ-function in $g(E)$. The highest electric fields are expected to occur at the two-phase interface. Inserting $E_{VH} = E_{\text{max}}$ into Eq. (5) gives the corresponding coordinates $(r = a^+, \theta = 0)$ and $(r = a^+, \theta = \pi)$. Notice that at $r = a$, the surface $|\mathbf{E}(\mathbf{r})|$ has finite jump due to the discontinuity in normal component of $|\mathbf{E}|$ given by (3).

The locations of the singularities $E_{VH} = |B||1 \pm \beta\phi_2|$ are not obvious. In this case, the solution of (5) are the curves

$$\theta = \pm \arccos\left\{\frac{1}{2}\beta\left[\frac{a^2}{r^2} - \frac{a^2 r^2}{b^4}\right] - (\pm)\frac{r^2}{b^2}\right\} + k\pi, \qquad (13)$$

$k = 0, \pm 1, \pm 2, \ldots$, and $r \in [a, b]$ which are plotted in Fig. 1(b). The dotted central curves correspond to $E_{VH} = |B||1 - \beta\phi_2| = E_0$. The field strength on the dashed curves is $E_{VH} = |B||1 + \beta\phi_2|$.

The case in which $\epsilon_2 < \epsilon_1$ can be studied using similar considerations. For example, the peak of the δ-function will be at $E_{VH} = E_{\text{max}}$ since the highest fields are always generated in the less conducting phase.

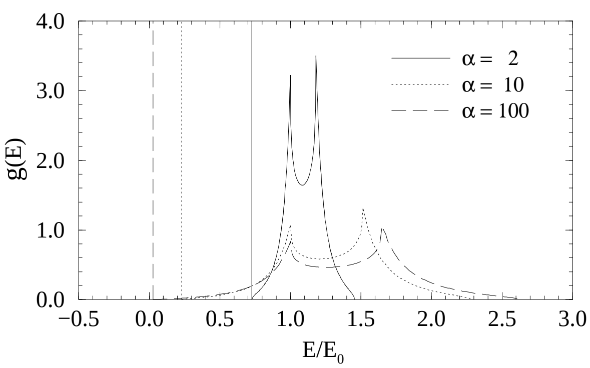

FIG. 2. Density of states $g(E)$ for the HS construction with at $\phi_2 = 0.25$ for contrast values $\alpha = \epsilon_2/\epsilon_1 = 2$, 10, and 100.

In Fig. 2, the density of states $g(E)$ of the composite cylinder model is plotted for several values of the contrast ratio $\alpha = \epsilon_2/\epsilon_1$, at fixed volume fraction $\phi_2 = (a/b)^2 = 0.25$. Increasing the contrast between inclusions leads to a broadening of $g(E)$. With an increase of α, the maximum field strength (in the less conducting phase) increases while in the higher conducting phase, the amplitude of the constant field decreases. The positions of van Hove singularities are easily identified as the minimum or maximum field, or local maxima in $g(E)$. In the opposite limit, $\alpha \to 1$, the bandwidth of the allowed fields collapses to the single peak $\sim \delta(E - |A|)$, as expected.

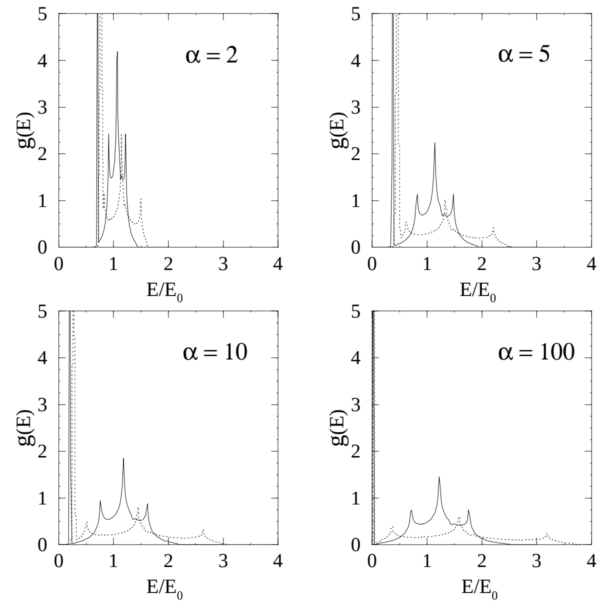

FIG. 3. Density of field states $g(E)$ for square arrays of cylinders for different contrasts $\alpha = \epsilon_2/\epsilon_1$, and different volume fractions: $\phi_2 \approx 0.2$ (full lines), 0.4 (dotted lines). Potential and electric fields are calculated by the finite difference method with resolution $L/400$, $L = 1$.

Next we extend our considerations to composite material with periodic microstructure. In particular, we consider a square array of cylinders of dielectric constant ϵ_2 in a matrix with dielectric constant ϵ_1: a model whose effective dielectric constant has been well studied [10,11]. Let the distance between the centers of neighboring cylinders be $2L$ and assume that the external field $\mathbf{E}_0$ is applied along the x-axis. Although analytical multipole expansion techniques (leading to an infinite set of linear equations which must be truncated) yield accurate estimates of the effective dielectric constant, they are not adequate to obtain the field distribution. Accordingly, we use the finite difference scheme to solve (1)-(3).

The essence of the numerical method is to map the composite to a network of conductors in which each conducting bond has the dielectric constant of the corresponding region in the composite. The potential fields at each internal node are solutions of the system of equation $\sum_j \epsilon_{i,j}(u_i - u_j) = 0$, where index j runs over the nodes which are the nearest neighbors of the node i, where $\epsilon_{i,j}$ is the dielectric constant of the bond between i^{th} and j^{th} node. In addition to these equations, macroscopic boundary conditions are imposed. Because of periodicity, it is enough to consider the solution in a square box of size L with a cylinder centered at one of

its corners. Then the boundary condition on the edges along the direction transverse to the applied field, say the y-direction, is $\partial_y u(x,y) = \partial_y u(x,y+L) = 0$. In the direction of the applied field, there is finite gradient $u(x+L,y) - u(x,y) = -E_0$.

The solutions for the density of states $g(E)$ are shown in Fig. 3. First we notice that in addition to the δ-function-like peak associated with the fields inside the cylinders, there are three prominent local maxima. These maxima are signatures of van Hove singularities. (Further details about the topological properties of the field surfaces will be given elsewhere [13].) The field fluctuations lie in the bandwidth of the density of states. Figure 3 illustrates how by increasing the phase contrast α, the fluctuations grow. It seen that the same effect is found if the volume fraction ϕ_2 increases toward the percolation threshold.

As a final example, we consider random arrays of cylinders whose density of states is distinctly different than the first two examples. Previous work on field fluctuations reveal distributions with two *global* (as opposed to local) peaks [5,7], although they arose for different reasons in these two studies. The presence of two global peaks is readily understood from our study as is explained below. In fact, we conjecture that random multiphase composites with widely different dielectric constants will have many well separated global peaks.

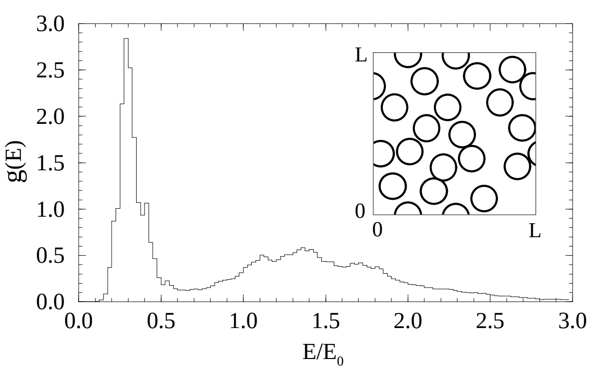

FIG. 4. Density of states for a single realization of a random dispersion of nonoverlapping cylinders (see inset) with $\alpha = 10$, $\phi_2 \approx 0.4$, calculated by a finite difference scheme with a resolution $L/400$.

Figure 4 shows the histogram of $g(E)$ that we have calculated for a single realization of a random distribution of 20 nonoverlapping disks of dielectric constant $\epsilon_2 = 10$ in a matrix of $\epsilon_1 = 1$. The system size is $L = 1$, so that the volume fraction $\phi_2 \approx 0.4$. Neglecting the irregularities due to insufficient statistics in the number of calculated fields, the positions of the three local maxima (van Hove singularities) at $|\mathbf{E}(\mathbf{r})|/|\mathbf{E}_0| \geq 1$ are still evident, although significantly diminished relative to the previous periodic example. Averaging [12] the density of states over many realizations of random samples, as was done in Refs. [5,7], additionally smears the sharpness of the band edges and maxima. Therefore, disorder causes the local maxima to broaden and eventually merge together, i.e., the local features disappear as the disorder increases. Similar disorder effects are well known in the theory of elecronic density of states in solids.

To summarize, we find van Hove type singularities in the density of states for local electric fields induced by an applied field in composites. We show how these singularities are related to the maxima and the bandwidth of $g(E)$. The complex multiple-peak behavior in the density of states are not adequately characterized by straightforward calculation of their lower moments. Analysis of $g(E)$ at its van Hove singular points represents a powerful new approach to quantify field fluctuations in composite media.

It is noteworthy that the density of states analysis of field fluctuations laid out in this paper for dielectric composites can be applied to other field phenomena, including strain fields in elastic media, velocity fields for flow through porous media, and concentration fields for diffusion and reaction in porous media.

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